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Gas–liquid reactor/separator: dynamics and operability characteristics

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Abstract

A comprehensive mathematical model is developed to simulate gas–liquid reactor in which both, reactants as well as products enter or leave the reactor in gas phase while the reactions take place in liquid phase. A case of first-order reaction (isothermal) was investigated in detail using the dynamic model and numerical bifurcation tools. Strong coupling between reaction kinetics and product removal rate was found to lead to complex dynamic (including over-flow/dry-up or oscillatory) behaviour. Key parameters controlling operability and dynamic characteristics were identified. Operability maps of the reactor/separator are presented. The model and results discussed will be useful for design and operation of industrial reactor/separators.

1. Introduction

In recent years, there is a growing interest (scientific as well as commercial) in the field of multifunctional reactors, which combine one or more unit operations with reaction. Such combined reactor/separators may lead to simpler processes, higher yields and lower energy consumption. The schematic of one of such gas–liquid reactor/separator is shown in Fig. 1. In such case, reactants are fed to the reactor in gaseous form. These reactants are transferred to the liquid phase containing non-volatile catalyst where they react to form volatile products. The products are transferred to the gas phase and are removed from the reactor in gaseous form. Depending on the relative rates of formation and removal of products, the liquid volume in the reactor may change and may exhibit complex dynamics. The strong coupling between reactions, heat effects and separation requires careful analysis of operability and dynamic characteristics of such multifunctional reactors.

Despite the commercial applications (for example, propylene hydroformylation, methanol hydrochlorination processes), the operability and dynamics of such gas–liquid reactor/separators have not been studied adequately. Most of the published studies on dynamics of gas–liquid reactors were limited to analysis of conventional gas–liquid reactors. None of these studies has examined influence of vapour–liquid equilibrium (VLE) on reactor dynamics. Hancock and Kenney (1977) have presented experimental data (as well as preliminary analysis) of oscillations observed in such gas–liquid reactor/separator. In this paper, we present a comprehensive model to describe dynamics and operability characteristics of gas–liquid reactor/separator. The scope of the present paper is restricted to a simple, first-order reaction carried out in an isothermal reactor/separator. The objective is to identify key variables and understand role of VLE in operability and dynamic characteristics. Experimental verification of models and tools discussed here for methanol hydrochlorination reactor/separator will be published separately.

2. Mathematical model

We consider here a gas–liquid reactor/separator with one incoming gas stream and one outgoing gas stream. Total number of gaseous components (combining products, reactants and inert) are n_k. The reactor liquid consists of finite amount of non-volatile component representing catalyst, ligands, etc. The reactants get dissolved in liquid phase and react. Overall mass balance of component k for the reactor/separator can be written as

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(V_L C_k + \frac{V_G P_k}{RT}\right) = \frac{V_i P_{ki}}{RT_i} - \frac{V_o P_k}{RT} + V_L R_k, \tag{1}$$

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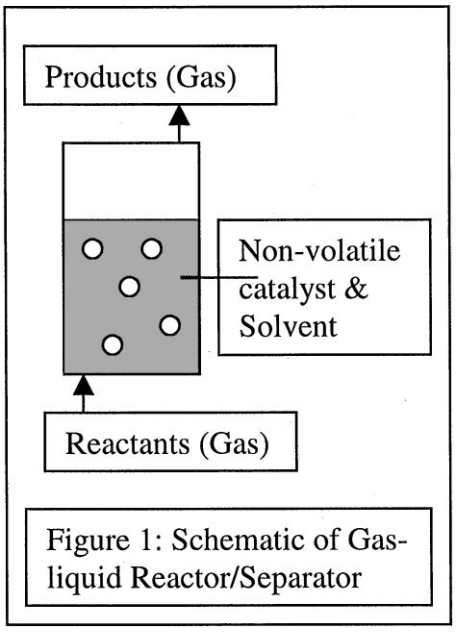

Fig. 1. Schematic of gas–liquid reactor/seperator.

where V_L and V_G are volume of liquid and gas phase, respectively, C_k and p_k are liquid phase concentration and gas phase partial pressure of component k, v is gas flow rate and R_k is the rate of formation of component k. Subscripts i and o denote inlet and outlet, respectively. Unlike Hancock and Kenney (1977), we have considered here accumulation in gas phase and the possibility of outlet gas flow rate different than the inlet gas flow rate.

In Eq. (1), there are $(2n_k + 3)$ unknowns appearing in n_k independent equations (n_k liquid phase concentrations, n_k partial pressures, volume of liquid phase, volume of gas phase and outlet gas flow rate). It is therefore necessary to formulate additional $(n_k + 3)$ equations to close the set. The volume of liquid and gas phase within the reactor can be related as

$$V_L + V_G = V_R, \tag{2}$$

where V_R is the reactor volume. The volume of liquid within the reactor can be calculated using the knowledge of non-volatility of catalyst and assumption of constant density of liquid as

$$V_L = \frac{m_c}{C_c}, \tag{3}$$

where m_c and C_c are amount of catalyst charged in the reactor and concentration of catalyst in the reactor liquid, respectively. Assumption of constancy of liquid density over the operating range of interest suggests the following:

$$\rho_L = M_c C_c + \sum (C_k M_k), \tag{4}$$

where M_k is molecular weight of component k. Eqs. (2)–(4) can be used to obtain values of liquid and gas volume in the reactor at any time, provided that liquid phase concentrations of n_k components are known. In the absence of mass transfer limitations, partial pressure of component k can be related to its liquid phase concentration using the equilibrium condition as

$$C_k = H_k p_k. \tag{5}$$

The coefficient H_k will in general, be a function of reactor temperature and liquid phase concentrations. The functional form of H_k was considered as

$$H_k = H_{Rk} f_k(C_1, C_2, \ldots, C_k, C_c) \exp\left(\frac{S_{1k}}{T + S_{2k}}\right), \tag{6}$$

where S_{1k} and S_{2k} represent temperature dependence (heat of solution or constants of Antoine equation for vapour pressure). For components following ideal Henry's law, the function f_k is unity and H_{Rk} is Henry's constant. For components following the ideal Raoult's law, f_k is equal to C_t and H_{Rk} is inverse of vapour pressure. Most of the industrial systems may deviate from ideal systems. All such deviations can be accommodated in the present framework by suitably modifying f_k. The set of n_k equations (Eq. (5)) can be used to relate partial pressures with liquid phase concentrations provided temperature is known. Temperature can be calculated by solving energy balance over the reactor. However, since the scope here is restricted to isothermal operation, temperature of the reactor/separator was an input parameter.

The gas out flow from the reactor was modelled using the proportional pressure regulator as

$$v_o = \alpha \left[\sum p_k - \left(P_{op} - \frac{v_i}{\alpha} \right) \right], \tag{7}$$

where α is the characteristic valve constant and P_{op} is the set point for the operating pressure of the reactor. This form ensures that when sum of partial pressures in the reactor equals the set operating pressure, gas out flow will be equal to gas in flow. The equation set is now closed and can be solved to simulate a dynamic behaviour of gas–liquid reactor/separator. The governing equations were made dimensionless (by defining suitable reference variables) before the solution.

3. Results and discussion

In most of the gas–liquid reactor/separators, non-volatile catalyst is dissolved in one of the products of the reaction. Two competing processes control the volume of liquid in the reactor: dissolution of reacting gases and reactions taking place in liquid phase will increase the liquid volume. Stripping of liquid phase by un-reacted gases will remove volatile products and reduce the liquid

Table 1
List of dimensionless parameters used in the simulations (if not stated otherwise)

Parameter	Value	Parameter	Value	Parameter	Value
Da	0.05	d	0.6	C_{AC}	1.0
b	0.0041	m_c	110.0	α	100.0
M_A	0.001	M_B	0.001	M_C	0.00325
H_{RA}	60.0	H_{RB}	0.060		

volume. Reactor volume poses an upper bound while the amount of non-volatile catalyst poses a lower bound on liquid volume in the reactor. We discuss here the dynamic behaviour of gas–liquid reactor/separator after describing details of considered system.

3.1. Considered reaction system and VLE

As mentioned earlier, we restrict the scope of investigation to a case of isothermal operation of a reactor/ separator carrying out a following simple reaction:

$$A \rightarrow B. \tag{8}$$

Pure A is fed in gaseous form to the reactor containing a non-volatile catalyst dissolved in B. Component A dissolves in liquid and reacts in liquid phase to produce B. Product B is removed from the reactor in gaseous form. The reaction kinetics was assumed to be a first order with respect to A and can be described in dimensionless form as

$$R_A = -DaC_A = -R_B, \tag{9}$$

where Da is Damkohler number defined as $k_1 t_{ref}$, k_1, is first-order rate constant and t_{ref} is the reference time (residence time). Reactant A was assumed to obey Henry's law. For most of the practical systems, vapour pressure of product B will be affected by dissolved catalyst as well as reactant concentrations in liquid phase. In general, dissolved non-volatile catalyst containing ionic species will decrease the vapour pressure of solvent B. The method of Kumar and Patwardhan (1986) can be followed to estimate the decreased vapour pressure, which will be function of ionic strength. For most of the practical systems, influence of non-volatile ionic species can be approximated as

$$P_B^o \propto (1 - bC_c), \tag{10}$$

where C_c is concentration of catalyst and b is an empirical parameter specific to a system.

In many cases, the product vapour pressure may also be a function of dissolved reactant concentrations. For example, in a methanol hydrochlorination system, vapour pressure of product water is strongly dependent on concentration of hydrogen chloride in liquid. Following the trends in experimental data reported by Hancock and Kenney (1972), the dependence of vapour pressure of B on concentration of A was represented as

$$P_B^o \propto \left\langle I, \left(\frac{C_A}{C_{AC}}\right)^{-d} \right\rangle, \tag{11}$$

where $\langle\ \rangle$ indicate minimum of the enclosed terms, C_{AC} denotes a critical concentration of A beyond which it starts affecting the vapour pressure of B and d is a system specific parameter. This form allows representation of ideal as well as strong deviations from Raoult's law behaviour. The data of methanol hydrochlorination system (Chen et al., 1970; Hancock & Kenney, 1972) indicate the values of parameter d in the range of 0–3. Thus, the operability and dynamics of gas–liquid reactor carrying out reaction (8) is controlled by eleven dimensionless parameters which are listed in Table 1.

3.2. Simulation of operation of reactor/separator

Unlike the classical nonisothermal CSTR, where relative rates of generation and removal of heat control the dynamics, in the reactor/separators considered here, main competing processes are generation of B within the reactor and removal of B from the reactor. For the specific values of Damkohler number, Da and other parameters, as volume of liquid increases, generation of B increases. It eventually attains a maximum limit corresponding to complete conversion of reactant A. The removal rate of B is a complex function of liquid volume since vapour pressure depends on catalyst concentration (and therefore, liquid volume) and concentration of A. The non-linearity of rate of removal with respect to liquid volume may lead to multiplicity and oscillatory behaviour. Ranade (1998) has reported the calculated profiles of generation and removal rates of B for the parameter values listed in Table 1 (these results are not included here for the sake of brevity). His results indicate that meaningful values of removal rate of B cannot be obtained for all the possible values of liquid volume in the reactor. Beyond certain value of d (that is beyond certain extent of deviation from Raoult's law), curves of generation and removal no longer intersect indicating unfeasible steady state. These steady-state calculations also indicate the possibility of obtaining two steady states

(one stable and one unstable) at very low values of Damkohler numbers. Though these steady-state calculations are useful for developing the feel and understanding of multiplicity, dynamic simulations of reactor operation are necessary to study unstable operation and oscillatory behaviour.

Dynamic behaviour of an isothermal gas–liquid reactor/separator carrying out reaction (8) can be described by two independent ordinary differential equations. We have selected liquid phase concentrations of A and B as the two primary independent variables. All the other quantities of interest like liquid volume, partial pressures of A and B can be related to these two primary variables. The mass balance (dimensionless) equations were rewritten as

$$\sum_{j=1}^{3n_k+2} a_{ij}\frac{dy_j}{dt} = b_i, \tag{12}$$

where y_j can be n_k liquid phase concentrations, n_k partial pressures, n_k values of effective Henry's coefficients, liquid volume and reactor temperature (that is $3n_k + 2$ variables). These $(3n_k + 2)$ linear equations were solved to calculate time derivatives of liquid phase concentrations. Integration of time derivatives was carried out using LSODA (of Petzold & Hindmarsh, 1982) routine which can handle stiff or non-stiff ordinary differential equations.

Typical predicted transient profiles of liquid volume in the reactor are shown in Fig. 2 for four values of coefficient, d (0, 0.4, 0.633 and 0.8). It can be seen that for the first two values of d (0 and 0.4), reactor attains the stable steady state. For $d = 0.633$, liquid volume in the reactor shows sustained oscillations with amplitude of about 0.02 and period of about 50 (dimensionless). As the value of d increases further, the oscillations become more prominent with significant increase in amplitude (about 0.4) and period of oscillations (about 500). These simulations clearly indicate that as non-linearity in VLE increases beyond certain extent, behaviour of the reactor changes qualitatively from stable steady operation to sustained oscillatory behaviour. Phase space plots for the case of $d = 0.633$ are shown in Fig. 3. It can be seen that reactor system converges to stable limit cycle by spiralling towards it.

3.3. Influence of system parameters and stability features

Dynamic simulations can give useful insight into behaviour of reactor. However, such simulations are rather cumbersome to use if one is interested in investigating influence of large number of parameters. Continuation techniques provide powerful tools to calculate parameter dependence of solutions of ODEs. These techniques can also be used to identify special points on the solution branches like limit points or Hopf bifurcation points. Basic concepts of continuation techniques are discussed in several books (for example, Seydel, 1988; Nayfeh & Balachandran, 1995). The governing model equations were rewritten in the form

$$\frac{du}{dt} - f(\mathbf{u}, \mathbf{p}, \lambda) = 0, \tag{13}$$

where $\mathbf{u}$ is vector of state variables, $\mathbf{f}$ is a vector of non-linear functions, $\mathbf{p}$ is vector of parameters and λ is a bifurcation parameter. A bifurcation diagram describes dependence of the state variable upon a continuous change in a bifurcation parameter, λ. A dynamic bifurcation analysis determines the critical value of parameter at which the dynamic features of the system change. A steady state becomes unstable and periodic solutions appear at a Hopf bifurcation point. In this work we have used a program AUTO (of Doedel, Champneys,

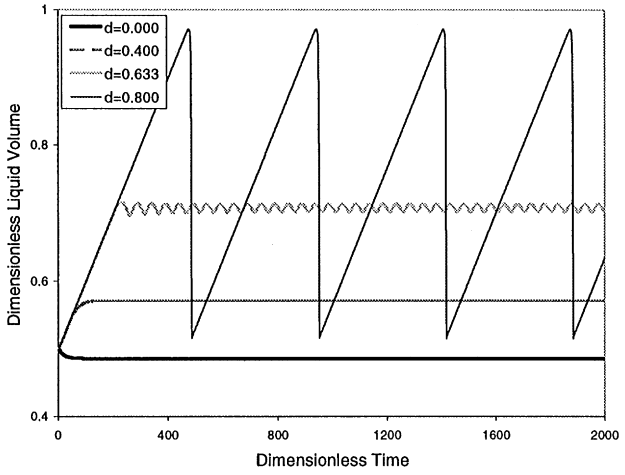

Fig. 2. Transient behaviour of reactor/separator.

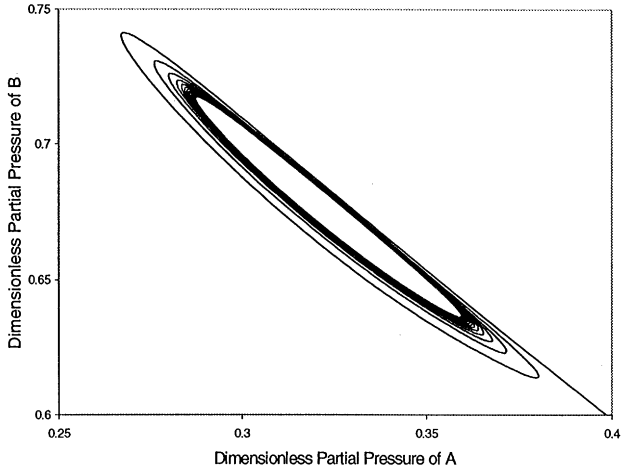

Fig. 3. Limit cycles for $d = 0.633$.

Fairgrieve, Kuynetsov, Sandstede & Wang, 1997), to carry out the bifurcation analysis of gas–liquid reactor/separator model discussed earlier. The results obtained by AUTO were validated by comparing those with the dynamic simulations discussed earlier.

The behaviour of the reactor/separator is determined mainly by three factors, namely: system properties (molecular weight, solubility and VLE, kinetics), design characteristics (reactor volume, outlet valve) and operating conditions (inlet gas flow rate and composition). In the present work, we have assumed inlet gas to be pure A. Molecular weights of the components and the catalyst and solubility were also fixed as listed in Table 1. AUTO was used to understand influence of three dimensionless parameters, namely, Damkohler number, *Da* (combines effect of kinetics and residence time); VLE parameter, *d* and amount of non-volatile catalyst charged in the reactor, m_c on behaviour of the reactor/separator.

Predicted variation of liquid volume in the reactor with Damkohler number is shown in Fig. 4 at five values of VLE parameter *d*. As expected, as Damkohler number increases, conversion of A and volume of liquid in the reactor increases. Increases in liquid volume is marginal and monotonous for zero or low values of *d*. As the value of *d* increases, profile of liquid volume exhibits a maxima with respect to *Da*. At sufficiently high values of *d*, stable steady-state solutions are no longer possible for all the values of *Da*. Reactor loses stability at certain critical values of *d* (Hopf bifurcation point, denoted by solid square) and may exhibit sustained oscillatory behaviour (denoted by dotted lines). Apart from identifying the location of Hopf bifurcation points, AUTO can also be used to calculate reactor behaviour beyond such Hopf bifurcation points. These computations indicate that as values of *Da* increase, period of oscillations increases up to a certain point and then levels out or even decreases slightly with further increase in *Da*.

It can also be seen that for certain combinations of *Da* and *d*, predicted steady-state liquid volume (dimensionless) in the reactor is greater than one, which indicates overflow conditions and infeasible operation. As value of *d* increases even further, the range of *Da* for feasible reactor operation shrinks rapidly. At higher values of *d*, reactor exhibits multiplicity but has a feasible operation for very low values of *Da* (liquid volume versus Da branch exhibit limit point: two solutions for $Da < Da_c$ and no solutions for $Da > Da_c$). Continuation techniques can be used to generate an operability map of the reactor/separator as shown in Fig. 5. The range of *d* values for which reactor will have sustained oscillations increases as value of *Da* increases. From the operating point of view, for a specific system (with fixed value of *d* and rate constant), increase in residence time may push the stable reactor operation into oscillatory behaviour or even to overflow and unfeasible operation. Operability map shown in Fig. 5 was obtained for specific values of parameters listed in Table 1. Several two-parameter maps can be constructed for the range of interest. An example of such a map with respect to Damkohler number and amount of catalyst is shown in Fig. 6 for two values of VLE parameter, *d*. Amount of catalyst present in the reactor has an upper bound determined by the molecular weight of the catalyst and density of liquid phase. For lower value of *d* (0.6), parameter space is divided into two regions corresponding to stable and sustained oscillatory behaviour (Fig. 6). For larger value of *d* (0.8), reactor exhibits overflow behaviour for higher values of catalyst present in the reactor. The region of oscillatory reactor behaviour increases with increase in the value of *Da*.

In reactor/separators discussed here, non-volatile, homogeneous catalyst is retained in the reactor for a long time. Its catalytic activity may decrease during this period. It is a common practice in industry to compensate such a decrease in catalyst activity by either increasing operating pressure or temperature. In general, these

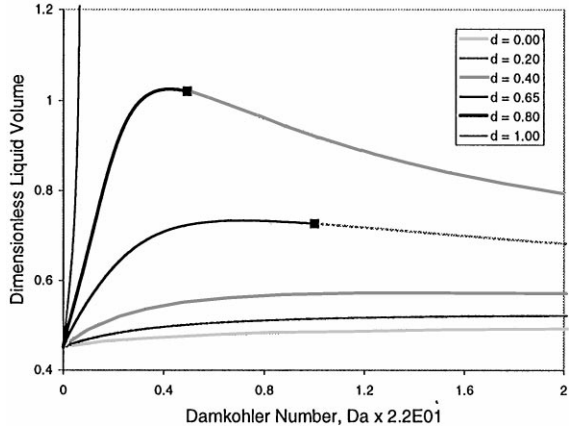

Fig. 4. Continuation results for 6 *d* values.

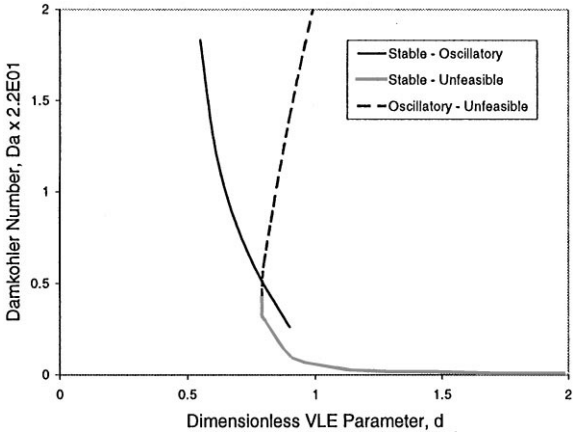

Fig. 5. Operability map, *Da*-*d*.

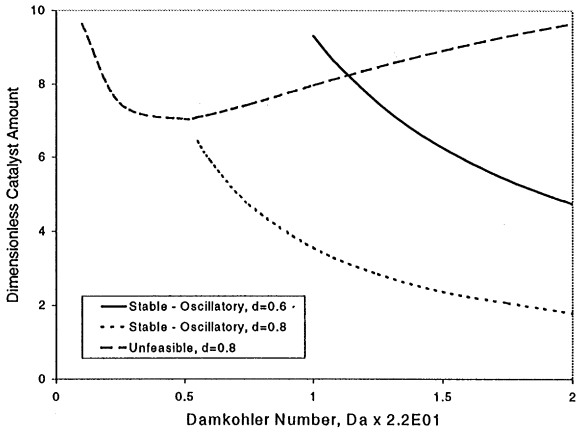

Fig. 6. Operability map, m_c-*Da*.

two options will have different effect on liquid hold-up. Increase in operating pressure or decrease in operating temperature will lead to decrease in removal rate of products and therefore will increase liquid hold-up in the reactor. For a specific reaction system, there will be an upper limit on operating pressure to avoid over-flow. Increase in temperature may lead to dry-up resulting in very low liquid hold-up and therefore lower conversions. Controlling the liquid hold-up in the reactor/separator is therefore one of the key design and operating objectives. The model, methods and results discussed earlier will be useful to achieve such an objective.

4. Conclusions

A comprehensive mathematical model was developed to simulate the gas–liquid reactor/separator. The rates of formation and removal of products (which are functions of reaction kinetics, VLE and residence time) control the behaviour of gas–liquid reactor/separator. Even for an isothermal operation, non-linearity in VLE was found to be sufficient to lead to an oscillatory or unstable behaviour of reactor/separator. The operation of reactor/separator may become infeasible due to over-flow or dry-up under certain conditions. The advantages of gas–liquid reactor/separator cannot be realised without a detailed understanding of dynamics of liquid hold-up in such reactor/separators. The models, tools and results described here will be useful in enhancing understanding of operability and dynamics of gas–liquid reactor/separators.

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